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Biodiesel production by ultrasound-assisted transesterification: State of the art and the perspectives

Vlada B. Veljković*, Jelena M. Avramović, Olivera S. Stamenković

Faculty of Technology, University of Niš, 16000 Leskovac, Bulevar oslobodjenja 124, Serbia

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ABSTRACT

In the present paper state-of-the art and perspectives of ultrasound-assisted (UA) biodiesel production from different oil-bearing materials using acid, base and enzyme catalysts are critically discussed. The ultrasound action in biodiesel production is primarily based on the emulsification of the immiscible liquid reactants by microturbulence generated by radial motion of cavitation bubbles and the physical changes on the surface texture of the solid catalysts generating new active surface area. The importance of ultrasound characteristics and other process variables for the biodiesel yield and the reaction rate is focused on. UA transesterification is compared with other techniques for biodiesel production. Several different developing methods reducing the biodiesel production costs such as the optimization of process factors, the development of the process kinetic models, the use of phase transfer catalysts, the application of the continuous process, the design of novel types of ultrasonic reactors and the *in situ* ultrasound application in transesterification of oily feedstocks are also discussed.

Contents

* Corresponding author.
E-mail address: veljkovicvb@yahoo.com (V.B. Veljković).

[1] Enzymes are large-molecular-weight proteins of colloidal size, 10–100 nm, so enzyme reaction systems represent a gray region between homogeneous and heterogeneous ones, and therefore enzyme-catalyzed transesterification reactions are separately discussed.

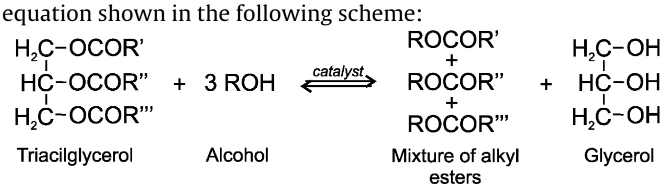
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1. Introduction

Several socioeconomic aspects and increased environmental concerns are driving industry to come up with an alternative fuel to fossil fuels, such as biodiesel. The main socioeconomic reasons are political instability of the greatest oil exporting regions, depletion of the world's oil reserves and increasing oil demand, which result in the oil price increase. From the environmental point of view, fossil fuels such as diesel are considered by most researches to be responsible for global warming phenomena.

Biodiesel is less toxic, biodegradable, sulfur free, reduces carcinogenic air toxins (particulate matter, unburned hydrocarbons, carbon monoxides and sulfates) by 75–90% compared to diesel [1,2] and can be used in any compression ignition engine without major modifications [3]. Biodiesel fuel is defined as the alkyl esters of long chain fatty acids, which fulfills certain standards, which is obtained by the transesterification or alcoholysis of natural triacilglycerols (TAG) such as vegetable oils, animal fats, waste fats and greases, waste cooking oils (WCO) or side-stream products of refined edible oil production with short-chain alcohols, usually methanol or ethanol.

The transesterification reaction requires the presence of a catalyst, which can be a base, an acid or an enzyme to occur at an acceptable rate, although it can be conducted in non-catalytic but supercritical conditions. Base and acid catalysts, most commonly used in biodiesel production, include both homogeneous and heterogeneous catalysts. Transesterification reaction is a sequence of three consecutive and reversible reactions, in which di- and monoacilglycerols (DAG and MAG, respectively) are formed as intermediates. It is often presented by the overall stoichiometric equation shown in the following scheme:



Since the transesterification reaction is reversible, an excess of alcohol is usually used to shift the equilibrium toward the formation of fatty acid alkyl esters (FAAE).

The major obstacle to large-scale commercialization of the biodiesel production is its high cost [4]. Therefore, much recent research has been focused on developing methods to reduce the biodiesel production cost. Among these methods is the development of novel reactor types that maximize the interfacial surface area between the two immiscible reactants to improve the performance of the reaction [5,6]. The majority of current biodiesel production methods employ batch reactor technology [7,8], which has limited capability for a number of reasons. Owing to the immiscibility of the reactants, the synthesis of biodiesel takes place at the interfacial surface area. Batch reactors utilize intense agitation to create and maintain a stable emulsion to minimize mass transfer limitations and to allow the reaction to reach kinetic equilibrium. If the agitation intensity is inadequate or the reaction temperature is low, homogeneous base-catalyzed transesterification reactions will suffer from the mass transfer limitation in the initial period [9]. Different intensification methods such as ultrasonic and microwave irradiation, hydrodynamic cavitation, addition of co-solvents or mass transfer catalysts and application of supercritical synthesis conditions have been tried out to eliminate or minimize the mass transfer limitation in order to improve the biodiesel production process.

Recent developments in sonochemistry allow the use of ultrasonic irradiation as a new, more efficient mixing tool in biodiesel production. US biodiesel production from various feedstocks is the focus of many research groups all over the world in the last decade. The use of low-frequency ultrasound (LFU) in biodiesel production has several advantages over the classical synthesis. LFU energy improves the mass transfer between the immiscible reactants via ultrasonic cavitation. It is not only efficient and time saving but also economically viable as it requires low quantity of catalyst [10] and only one-third to a half of the energy that is consumed by mechanical agitation [11–13]. Maximizing the interfacial surface area between the immiscible reactants at lower energy inputs than conventional stirred reactors, ultrasonic reactors might be attractive for improving the performance of the transesterification process by obtaining higher biodiesel yields within shorter reaction times. Since the energy required for the biodiesel production represents a significant part of the overall energy input, the use of ultrasonic reactors with better performances than currently employed can reduce the production cost, enhancing chances for large-scale commercialization of the biodiesel production.

In the present paper state-of-the art and perspectives in the use of ultrasound in biodiesel production from different oil-bearing materials using acid, base and enzyme catalysts are critically analyzed. At first, the physical basis and possible ultrasound actions in both homogeneous and heterogeneous reaction systems are shortly explained. Then, the importance of ultrasound characteristics (power, amplitude, frequency and cycle) and other process variables (alcohol-to-oil molar ratio, catalyst loading, mixing intensity, reaction temperature and reaction time) for the biodiesel yield and the reaction rate is focused on. Further, UA transesterification is compared with other methods for biodiesel production to highlight their advantages and disadvantages. Finally, several different developing methods reducing the biodiesel production costs are discussed. The special attention is paid to novel types of ultrasonic reactors with better performances than currently used.

2. The physical basis of the ultrasound action

The term sonochemistry refers to the use of ultrasound to chemical reactions and processes such as food processing, stabilization of oil emulsions, particle size reduction, filtering systems for suspended particles, homogenization, atomization, environmental protection, etc. Ultrasound is a sound of a frequency higher than that the human ear can respond. According to its frequency, ultrasound is classified into high-frequency (2–10 MHz) and low-frequency (20–100 kHz) ultrasound [14]. Nowadays, LFU is more and more present in all areas of chemistry and chemical technologies. It successfully increases the conversion, improves the yield, changes the reaction pathway and initiates the reaction in many biological, chemical, and electrochemical systems. In organic synthesis, the use of ultrasound can reduce the number of synthesis steps, the reaction time and the reaction temperature.

The energy of ultrasonic irradiation can activate various mechanisms to affect positively chemical reactions and processes, which are not always known. These positive effects of ultrasound are generally attributed to so-called ultrasonic cavitation, which means the formation, growth and implosive collapse of bubbles (cavities) in a liquid irradiated with ultrasound. When ultrasound passes through the liquid, it consists of both expansion (negative pressure) and compression (positive pressure) waves. These form bubbles, filled with solvent and solute vapor and dissolved gases, which grow and recompress. Under proper conditions, ultrasonic cavitation leads to implosive cavitation bubble collapse, producing intense local heating, high pressures and very short lifetimes. The collapse of the cavitation bubbles gives rise to acoustic microstreaming or formation of small eddies that increase the mass and heat transfer in the liquid, and cause velocity gradients that result in shear stresses [15].

Generally, ultrasound can have physical and chemical effect on heterogeneous reaction systems through cavitation bubbles [14].

The former emulsifies immiscible liquid reactants by microturbulence generated because of radial motion of cavitation bubbles, and the latter is due to the production of free radicals during the transient cavitation bubble collapse. The increase in the interfacial area between the immiscible reactant enhances the reaction rate in the same way as in mechanically agitated reactors while free radicals formed to induce and/or accelerate chemical reaction in the bulk reaction mixture.

Most researchers believe that physical effect of ultrasound on the formation of the fine emulsion between immiscible fluids is responsible for accelerating the transesterification reaction. Collapse of cavitation bubbles generates microturbulence, disrupts the phase boundary and causes emulsification of alcohol into the oil phase by ultrasonic jets that impinge on one liquid to another. Once such an emulsion is formed, the surface area available for the reaction between the two phases significantly increases, thus accelerating the reaction [16]. A few researchers have reported that ultrasonic cavitation provides not only the mechanical energy for mixing but also the required activation energy for initiating the transesterification reaction [17]. Similarly, some of the researchers believe that the increase in the temperature at the phase boundary due to ultrasonic cavitation enhances the transesterification reaction [18,19]. However, according to Kalva et al. [20], chemical effect of ultrasound, i.e. free-radical production which would accelerate the reaction, does not seem to play any role in base-catalyzed soybean methanolysis carried out under 20 kHz ultrasound at the ambient temperature (27 °C).

As already said, in heterogeneous liquid–liquid systems, the cavitation bubble collapse at or near the interface cause disruption of phase boundary and mixing, resulting in the formation of fine emulsions, increase of the contact surface area between the two liquid reactants and enhancement of the reaction rate [16]. These emulsions usually have drops smaller in size and are more stable than those obtained using conventional techniques, which is very beneficial for liquid-liquid reaction systems. In heterogeneous solid–liquid systems, cavitation events at or near the surface of catalyst particles cause the formation of liquid jets at solid surfaces by the unsymmetrical inrush of the fluid to the voids and may reduce particle size leading to increased surface area [21]. These jets increase the mass transfer from the bulk of the liquid phase to the catalyst surface by the disruption of the liquid boundary layer. Also, they can activate the solid catalyst and dislodge the materials occupying the inactive sites. Similarly, in heterogeneous solid–liquid–liquid systems ultrasound can increase the surface area for a reaction, the mixing intensity and the mass transport rate. However, ultrasound irradiation may cause the leaching of some solid catalysts at high catalyst loadings [22].

3. The use of ultrasound in biodiesel production

Ultrasound has been employed in transesterification reactions catalyzed by acid, base or enzyme catalysts. In these processes, vegetable edible and non-edible oils are mostly used although oil-bearing materials such as seeds [23–25], rice bran [26] waste cooking oils [27–30], fish oils [31,32], animal fats [33] and side-streaming products from edible oil production [34] have been also employed as feedstocks. In some studies, pure acids such as oleic [35], caprylic and capric [36] acids as well as pure triolein [37–39] have been utilized. In UA transesterification reactions, batch and flow reactors with indirect or direct sonication are used. The former sonication is performed in a reaction vessel (usually Erlenmeyer or round-bottom flask) immersed in an ultrasonic cleaning bath and the latter is a reaction vessel with an ultrasonic processing probe, known as horn (in the USA), sonotrode or sonoprobe, which is immersed in the reaction mixture. Two sonication modes are used, either pulse (some time on and some time off) or continuous. LFU is mostly used for sonication in biodiesel synthesis.

3.1. Homogeneously catalyzed transesterification

3.1.1. Acid catalysis

The most often acids used in transesterification are sulfuric and sulfonic acids. Acid-catalyzed transesterification is generally carried out at high alcohol-to-oil molar ratios, higher temperatures and high acid catalyst concentrations in order to obtain good biodiesel yields in practical reaction times. The homogeneous acid-catalyzed reaction is about 4000 times slower than the homogeneous base-catalyzed reaction [40]. Acid catalysts give very high yields in alkyl esters, but the reactions are slow, requiring, typically, temperatures above 100 °C and more than 3 h to reach complete conversion [40]. The acid-catalyzed transesterification is very useful for handling oils or fats with high free fatty acids (FFA), because acid catalysts can simultaneously catalyze both esterification and transesterification. The additional advantage of acid-catalyzed transesterification over base-catalyst method is that soaps are not formed in the presence of acid catalysts [41].

Ultrasound has been applied in a few studies of acid-catalyzed esterification and transesterification of different feedstocks in batch reactors, which are reviewed in Table 1. The use of ultrasound significantly reduces the reaction conditions of transesterification [17,32]. Only sulfuric and p-toluenesulfonic acid has been used as a catalyst. Hanh et al. [35] and Santos et al. [32] have carried out UA sulfuric acid-catalyzed esterification of oleic acid with short chain alcohols and FFA from *Oreochromis niloticus* oil with methanol, respectively, and reported the ester yields higher than 95% under the optimum reaction conditions. Ethyl ester conversion increases rapidly with increasing the ethanol-to-oleic acid molar ratio from 1/1 to 3/1, where it reaches the maximum, after which gradually decreases [35]. The most important factor affecting the reaction is the alcohol-to-FFA molar ratio [32]. Kelkar et al. [36] performed acid-catalyzed esterification of WCO (C_8–C_{10} fatty acid odor cut) with methanol at optimal reaction conditions, and reported conversion levels of higher than 98% in 75 min. With increasing alcohol-to-oil molar ratio from 5/1 to 10/1, the yield was increased from about 91% in 3 h to about 98% in 2 h. Lifka and Ondruschka [13] reported a very low methyl ester yield in 3 h of p-toluenesulfonic acid-catalyzed methanolysis of rapeseed oil. Deshmane et al. [34] carried out acid-catalyzed methanolysis of palm fatty acid distillate (PFAD), a side streaming product of palm oil production, under ultrasonic irradiation. At methanol-to-PFAD of 5/1, 5% of H_2SO_4 and 50 °C, the equilibrium conversion was enhanced from 65% in 7 h under stirring to 75% in 6 h of reaction time under ultrasonic irradiation. Thus, the use of ultrasound enhances the reaction rate and also shifts the equilibrium which results in higher product yields in shorter reaction times. The increase of the acid catalyst loadings from 0.5 to 0.75% increases the conversion to the maximum of ≥98%, and further increasing the catalyst loading causes a slight decrease of the conversion of coconut oil into biodiesel [42]. Also, the ethyl ester conversion increases with the increase in H_2SO_4 concentration up to 5%, after which it becomes constant [35]. With increasing the temperature from 10 to 60 °C in the case of acid-catalyzed esterification of oleic acid under ultrasonic irradiation, ethyl ester conversion increased and the time for the obtaining the maximum conversion shortened [35]. However, investigating the acid catalyzed synthesis of isopropyl esters from PFAD in the presence of ultrasonic irradiation, Deshmane et al. [34] observed that the reaction rate as well as the equilibrium conversion rapidly increased with an increase in the temperature from 30 to 50 °C.

Table 1
A review on the UA acid-catalyzed alcoholysis and esterification of different feedstocks in batch reactors: indirect sonication.

Frequency/power	Feedstock	Alcohol	Alcohol-to-oil molar ratio (mol/mol)	Temperature (°C)	Catalyst/loading (wt%)	Yield (%)/time (min)	Optimal reaction conditions		Reference
							Operation conditions	Yield (%)/time (min)	
40 kHz/1200 W	Oleic acid	Ethanol Propanol Butanol	1/1–10/1	10–60	H_2SO_4/0.5–10	na[a]/600	3/1 alcohol/oleic acid, 5% H_2SO_4, 60 °C	~95/120 ~92/120 ~85/120	[35]
40 kHz/60 W	FFA from *Oreochromis niloticus*	Methanol	3/1–9/1	25	H_2SO_4/0.5–2.0	98.2/90	9/1, 2%, 30 °C	98.2/90	[32]
20 kHz/120 W	C_8–C_{10} fatty acid cut	Methanol	5/1, 10/1	40	H_2SO_4/0.5–10	98/120	10/1,2% H_2SO_4	98/75	[36]
	Caprylic acid								
	Capric acid		10/1		Superacid clay (chlorosulfonic acid supported on zirconium)/ 1.0, 2.0	 75/300 97/420	10/1, 2% clay, 40 °C	97/420	
20% power (4 W)	Rapeseed oil	Methanol	3.3/1	45	p-Toluenesulfonic acid/3.75	11.6/180	–	–	[13]
25 kHz/1000 W	Palm fatty acid distillate	Isopropyl	3/1, 5/1, 7/1, 9/1	30–60	H_2SO_4/5		5/1, 5%, 60 °C	80/360	[34]

[a] na – not available.

3.1.2. Base catalysis

The main reason why base-catalyzed transesterification has been more popular for commercially purposes than acid-catalyzed one is that the former is much faster than the latter. Alkaline metal alkoxides and hydroxides are most often used base catalysts. The former are considered to be the most active catalysts, since they give very high yields (>98%) in short reaction times (30 min) even if they are applied at low concentrations (0.5 mol%). Alkaline metal hydroxides (sodium hydroxide and potassium hydroxide) are less active, but most usually used due to their low cost. These catalysts are used under low reaction temperatures and pressures, and the conversion rate is high with no intermediate steps [3]. The presence of FFA and water strongly affects the process performance and economics of biodiesel production via base-catalyzed transesterification. Oils used in alkaline transesterification should contain no more then 1% of FFA; otherwise saponification impedes the separation of esters and reduces the yield and formation rate of fatty acid esters. The presence of water affects the process of saponification, reduces the catalyst activity, increases the viscosity of the reaction mixture and causes the formation of stable emulsion, hindering the separation of the resulting glycerol [40]. Therefore, sodium and potassium hydroxide should be properly handled because they, as highly hygroscopic, absorb water from air during storage and can form water when dissolved in the alcohol, even if a water-free alcohol/oil mixture is used [3,43]. Also, water produced by the reaction of the hydroxide with the alcohol enhances hydrolysis of some of the produced ester, and causes soap formation.

Many researchers have succeeded in speeding up the reaction rate by carrying out homogeneous base-catalyzed methanolysis in the presence of LFU, for instance, Georgogianni et al. [23,24], Ji et al. [12], Lifka and Ondruschka [13], Siatis et al. [25], Stavarache et al. [10,44,45], etc. The effect of high-frequency ultrasound on the biodiesel production from soybean oil using methanol and potassium hydroxide as catalysts has been studied only by Mahamuni and Adewuyi [46,47]. The reviews of the studies on homogeneous base-catalyzed transesterification of various feedstocks with methanol or ethanol, mainly in the presence of sodium or potassium hydroxide as a catalyst at different initial loadings in batch reactors under indirect and direct sonication are given in Tables 2 and 3, respectively. Generally, the maximum biodiesel yields higher than 90% are obtained under the optimum reaction conditions within 3–30 min. The main operational factors affecting UA transesterification are: ultrasound characteristics (amplitude and frequency of ultrasound wave, i.e. ultrasonic energy, mode of sonication), type of alcohol, type of oil, alcohol-to-oil molar ratio, type and quantity of catalyst and the reaction temperature.

Ultrasonic energy is applied at different amplitudes in pulse and continuous sonication modes. Both the ultrasound wave amplitude and the sonication time in pulse mode affect the biodiesel yield [11,18,42]. There is the optimum amplitude and sonication time ensuring the highest biodiesel yield. In pulse mode (5 s on/25 s off), the highest biodiesel yield of 96% is obtained in 90 s, and in the continuous sonication mode, only 86% conversion is achieved in 15 s [11]. Of three amplitudes, the middle one (120 μm) in pulse mode ensured the highest biodiesel yield [11]. In the continuous sonication mode, the ultrasound wave amplitude greatly affects the transesterification reaction. An increase in the ultrasound wave amplitude results in increasing the biodiesel yield (>95%) at 5 min after the beginning of the soybean oil methanolysis catalyzed by KOH [17]. The prolonged reaction (10 min) results in higher biodiesel yields only at lower amplitudes, while at higher amplitudes biodiesel yields are reduced drastically due to cracking and degradation of fatty acid methyl esters (FAME). In order to obtain a maximum yield near 97%, input ultrasonic energy should be between 125 and 215 kJ [17]. The ultrasound wave frequency seems to affect the reaction rate and the biodiesel yield. Stavarache

Table 2
A review on the UA homogeneous base-catalyzed alcoholysis of different feedstocks in batch reactors: indirect sonication.

Frequency/power[a]	Feedstock	Alcohol	Alcohol-to-oil molar ratio (mol/mol)	Temperature (°C)	Catalyst/loading (wt%)	Yield (%)/time (min)	Optimal reaction conditions		Reference
							Operation conditions	Yield (%)/time (min)	
28 and 40 kHz; 400 W	Neat vegetable oil; edible grade	Methanol	6/1	25	NaOH/0.5, 1.0, 1.5	75–98/10–40	40 kHz, 0.5% NaOH	98/20	[54]
28 and 40 kHz, 60% power (720 W)	Vegetable oil, commercial edible oil	Methanol	6/1	36 ± 2	NaOH/0.5, 1.0, 1.5	75–98/10–40	40 kHz, 0.5% NaOH	98/20	[10]
					KOH/0.5, 1.0, 1.5	92–96/20–40	40 kHz, 0.5% KOH	96/20	
		Ethanol				30–88/10–50	40 kHz, 0.5% NaOH	88/20	
		Isopropanol				75–92/10–20	28 kHz, 0.5% NaOH	92/20	
		Isobutanol				87–99/40	40 kHz, 1% NaOH	99/40	
		Tertiary-butanol				No conversion	–	–	
40 kHz, 70% power (840 W)	Vegetable oils: canola, corn, grape, palm, sesame; commercial edible oil	Methanol	6/1	36 ± 2	KOH/0.5	na[b] >90/10	–	–	[44]
33 kHz	Soybean oil	Methanol	6/1	–		88/18	–	–	[101]
24 kHz, 200 W	Sunflower seed oil	Methanol Ethanol	7/1	60 80	NaOH/ 1.0, 1.5, 2.0	69–95/5–60 39–90/5–60	2% NaOH	95/40 90/60	[24]
40 kHz, 4870 W/m^2	Soybean oil	Methanol	3/1, 6/1, 9/1	29	NaOH/ 0.20, 0.40, 0.60	52–100/30	9/1, 0.2% NaOH	100/30	[19]
40 kHz, 4870 W/m^2	Soybean oil	Ethanol	3/1–9/1	29	NaOH/0.2–0.5	–	10.2/1, 0.35% NaOH	91.8/30	[102]
323, 581, 611, 1300 kHz; 13–223 W[a]	Soybean oil	Methanol	4/1, 6/1, 7.5/1, 9/1, 12/1	20, 26, 27, 35 ± 1	KOH/ 0.1, 0.3, 0.5, 0.6, 1	50–95	611 kHz, 139 W, 6/1, 26 ± 1, 0.5% KOH	>95/15	[46]
20 kHz, total power 85 W	Soybean oil Castor oil Peanut oil		4/4 (w/v)	na	NaOH/0.5, 1.0	97/15 99/10 99/10	–	–	[16]
24 kHz, 200 W	Cottonseed oil	Methanol Ethanol	7/1	60 80	NaOH/ 1.0, 1.5, 2.0	71–95/5–20 52–90/10–60	2% NaOH	95/20 90/60	[23]
400 Hz–400 kHz	Peanut oil	Methanol	3/1, 6/1, 9/1	25	KOH, NaOH, KOCH$_3$, NaOCH$_3$/0.5–3%	~90/60	6/1, 1% KOH, 40 kHz	~90/60	[52]
40 kHz	Crude cottonseed oil	Methanol	0.95/1, 3/1, 6/1, 9/1, 11/1	25	NaOH/0.5, 1.0, 1.5, 1.8	10–98/0.43–15.57	6.2/1, 1% NaOH	~98/8	[77]
35 kHz	Fish oil	Ethanol	6/1	20, 60	KOH/0.5, 0.75, 1.0	98.1/90	6/1, 1% KOH	92/10	[31]
40 kHz, 1200 W	Triolein	Methanol	6/1	3–50	NaOH, KOH/1	–	–	–	[37]
40 kHz, 1200 W	Triolein	Methanol	3/1,4/1,5/1, 6/1,9/1	25	KOH/0.5,1.0,1.5,3.0	Max/30	6/1, 1% KOH	–	[38]
40 kHz, 1200 W	Triolein	Methanol	6/1	25	NaOH, KOH/1.0	90/5	–	–	[39]
		Ethanol				90/5			
		Propanol				80/5			
		Butanol				80/5			
		Hexanol				73/5			
		Octanol				72/5			
		Decanol				70/5			

[a] Transducer out of the reaction vessel.
[b] na – not available.

Table 3
A review on the UA homogeneous base-catalyzed alcoholysis of different feedstocks in batch reactors: direct sonication.

Frequency/power[a]	Feedstock	Alcohol	Alcohol-to-oil molar ratio (mol/mol)	Temperature (°C)	Catalyst/loading (wt%)	Yield (%)/time (min)	Optimal reaction conditions		Reference
							Operation conditions	Yield (%)/time (min)	
20 kHz; 14.5 W	Soybean oil	Methanol	3/1, 4.5/1, 6/1,9/1	25, 40, 60	KOH/ 1.5, 2.2	82–92/3	6.0:1, 40 °C, 1.0% KOH	99.4/15	[48]
		Ethanol 1-Butanol 2-Propanol	6/1	60	KOH/1.5	99.11/120 92.02/120 29.21/120			
Pulse frequency: 0.4, 0.7, 1.0; 100, 150, 200 W	Soybean oil	Methanol	3/1, 5.5/1, 6/1	25, 35, 45	NaOH, KOH/ na	69–100/30	Pulse frequency 1.0, 100 W, 6/1, 45 °C	100/10–20	[12]
24 kHz; pulse 100%; amplitude 25, 50,75 and 100%; 400 W	Soybean oil	Methanol	6/1	64–149	KOH/1		Amplitude 100%, 89 °C	99/5	[17]
20 kHz, total power 2200 W	Soybean oil	Methanol	5/1	40	NaOH/ approx. 1	87–96/2.5	Amplitude 120 μm_{pp} in the pulse mode	95/1.5	[11]
20, kHz, total power 600 W	Soybean oil	Methanol	6/1	30	NaOH/1	90.2/10	–	–	[75]
24 kHz/200 W	Coconut oil	Ethanol	4/1, 5/1, 6/1		KOH/0.5,0.75, 1.0,1.25	>98/7	6/1, 0.75% KOH Amplitude 60%, Pulse 0.3 s/s c	>98/7	[42]
24 kHz, 200 W	Sunflower oil	Methanol Ethanol	7/1	60 80	NaOH/1.0, 1.5, 2.0	–	2.0% NaOH	95/20 90/20	[55]
20% power (4 W)	Rapeseed oil	Methanol	3.3/1	45	NaOH/ 0.5, 1.0	>80/20	0.5% NaOH	80/20	[13]
24 kHz, 200 W	Rapeseed oil	Methanol	7/1	60	NaOH/ 1.0, 1.5, 2.0	–	2.0% NaOH	96/20	[53]
20 kHz; 50% power (1040 W)[b]	Canola oil	Methanol	1/1, 2/1, 3/1, 4/1, 6/1	25 ± 2	KOH/ 0.3, 0.5, 0.7,1.0	>90/20–50	5/1, 0.7% KOH	99/50	[51]
20 kHz/100 W	Domestic and restaurant WCO	Methanol	3/1,6/1,9/1	25, 65	KOH/0.5,1.0	98–99/60	6/1, 1% KOH 65 °C Amplitude 100%	97.68–98.26/5	[29]
20 kHz/150 W, 200 W and 250 W	WCO	Methanol	4/1, 5/1, 6/1	35, 45, 55	KOH/0.5,0.75, 1.0,1.25	46–89.5/40	6/1, 1% KOH 45 °C, 200 W/40 min		[28]
20 kHz	Fish oil	Ethanol	6/1	20,60	C_2H_5ONa/0.8	>98/30	6/1, 0.8% C_2H_5ONa	>98/30	[31]
24 kHz/400 W	Beef tallow	Methanol	6/1	60	KOH/0.5	70 s	Power 100%		[33]

[a] Ultrasonic processing probe in all studies.
[b] With circulation.

et al. [10] has reported that at catalyst (NaOH) loadings lower than 1%, 40 kHz ultrasound is more effective in shortening the reaction time, but 28 kHz ultrasound gives slightly higher biodiesel yields. Since there are no significant differences in the cavitation bubble formation at the two frequencies, the difference in the biodiesel yield is attributed to difficulties through washing of product, a part of which remains trapped in the micelles. High-frequency ultrasound has a negligible influence on the biodiesel yield in the range of between 581 and 1300 kHz, while an increase in ultrasonic energy from 46 to 143 W enhances the biodiesel yield [46].

Methanol and ethanol are mainly used in UA transesterification of vegetable oils, although some other short-chain alcohols (C_3 and C_4) have been also used. Reactivity of alcohols decreases with increasing the number of C atoms in their molecules. More acidic alcohols react rapidly with base catalyst to form an alkoxide, while the secondary and tertiary alcohols react more slowly, probably due to the sterical hindrance [10]. Colucci et al. [48] reported that methanol and ethanol gave higher biodiesel yields (99%) than 1-butanol (92%) or 2-propanol (29%). Also, Hanh et al. [39] reported higher conversion of triolein with methanol and ethanol than with higher n-alcohols (C_3–C_{10}) and little ester conversion with the secondary alcohols (C_3–C_8). On the other side, increasing the chain length, the miscibility between oil and alcohol increases, thus enhancing reaction rate but making the separation of esters formed difficult [10].

The type of vegetable oil seems to affect both the biodiesel yield [45] and the reaction kinetics [49], which is attributed to various fatty acids present in different concentrations in various oils. UA base-catalyzed methanolysis of vegetable oils with a high percentage of linoleic acid follows the second-order reaction kinetics, while for the oils with higher contents of palmitic and oleic acids it is the second-order reaction only in the initial period [49].

Affecting the viscosity of the reaction mixture and the esters yield, the alcohol-to-oil molar ratio is one of the most important variables that affect fatty acid ester formation. As for transesterification in the absence of ultrasound, an excess of alcohol over the stoichiometric is required to maximize the biodiesel yield. The optimal reaction conditions for base-catalyzed transesterification involve alcohol-to-oil molar ratio 6/1 [48,50] or 5/1 [51]. The further increase in the alcohol-to-oil molar ratio did not affect the equilibrium conversion degree but only complicated ester and glycerol recovery, and thus increased the costs of the process [28,36,48]. Colucci et al. [48] showed that alcohol-to-oil molar ratio had a major effect on the percentage of FAME formation in the temperature and alcohol-to-oil molar ratio ranges of 25 to 60 °C and 3/1 to 6/1, respectively. The biodiesel yield in coconut ethanolysis increased from 84.9 to 94.2% when ethanol-to-oil molar ratio increased from 4/1 to 6/1; further increase of the ethanol-to-oil molar ratio did not increase the yield [42]. Hanh et al. [38] also reported optimal methanol-to-triolein molar ratio of 6/1, where the maximum of methyl esters was achieved. However, Fan et al. [52] observed for sodium hydroxide catalyzed methanolysis of crude cottonseed oil that FAME yield increased with the increase of the molar ratio from 3/1 to 6/1, after which the yield decreased.

Although alkoxide catalysts give higher yields of biodiesel due to the direct formation of alkoxide ions avoiding the generation of water as a by-product, in the case of base-catalyzed transesterification, sodium and potassium hydroxide are the first choice, due to their low price and easy handling. Ultrasonication allows the use of lower amounts of the catalysts due to the increased chemical activity [42]. There are no great differences in the time to complete conversion between sodium and potassium hydroxide [10]. However, Fan et al. [52] observed that biodiesel yields were higher when cottonseed oil methanolysis was catalyzed by potassium hydroxide than by sodium hydroxide, and also higher in the case of base methoxides than corresponding hydroxides. Over the range of 0.5–1.5% (w/w) of oil, the biodiesel yield is high when potassium hydroxide is used independently of its concentration and decreases with increasing the sodium hydroxide concentration [10]. At higher potassium hydroxide concentrations than 1% (up to 3%), the excessive amount of catalyst reduces the biodiesel yield and complicates the separation [52]. Both catalysts form soaps, but sodium soap favors the formation of emulsions in the washing step, thus hindering the purification and decreasing the biodiesel yield. By increasing base catalyst loading, FAME yield and reaction rate also increase [46], but the excess catalyst negatively affects FAME yield [10,19,23,53], due to the formation of the emulsion which increases the viscosity and induces the formation of the gel [50] that traps the formed esters and makes difficult the glycerol separation. The reaction in the presence of sodium hydroxide at the concentration of 1.0% [13], 1.5% [10,54] or 2.5% [23,24,53,55] and potassium hydroxide at 1.25% [28] and 1.5% [38] is followed by the strong soap formation, decreasing the FAME yield.

The reactions are usually carried out at temperatures lower than 60 °C and close to the ambient temperature. The temperature positively influences the biodiesel yield nearly up to the boiling point of alcohol if other parameters are kept unchanged [50]. Temperatures near the boiling point of alcohol cause the condition that dramatically reduces the cavitation and the efficiency of the reaction [56]. Increasing the temperature, the viscosity of the vegetable oils reduces, resulting in the increase in cavitation events and the rate of the emulsion formation [46], i.e. a decrease in viscosity reduces the cavitation threshold, which leads to increase the degree to which cavitation occurs [57]. Using the methanol-to-oil molar ratio of 3/1, Colucci et al. [48] observed that the increase in temperature from 25 to 60 °C slightly decreases the equilibrium FAME yield but not necessarily at higher molar ratios.

3.1.3. Two-step process

In the case of oily feedstocks containing high FFA, when a homogeneous base catalyst is used, soaps are produced in the reaction between the catalyst and FFA, which inhibit biodiesel production. If a homogeneous acid catalyst is used, the saponification reaction is avoided but the transesterification rate is slow. To overcome these disadvantages of homogeneous base and acid catalysts, a two-step process combining acid-catalyzed esterification and base-catalyzed transesterification appears to be an acceptable solution. This two-step process with ultrasonic irradiation was shown to be effective and time-saving for biodiesel production from *Jatropha* oil at 60 °C [58]. In one-step processes biodiesel yields were 47.2% (with a saponification problem) and 92.8% (with prolonged reaction time, 4 h) when sodium hydroxide and sulfuric acid were used as a catalyst, respectively, while in the two-step process, the biodiesel yield of 96.4% was achieved in 1.5 h.

3.2. Heterogeneously catalyzed transesterification

The use of heterogeneous catalysts significantly simplifies the process of separation and purification of the products, reduces environmental problems, allows reuse of the catalyst and contributes to positive economic effect [59]. Heterogeneous catalysts, such as strong acids and immobilized enzymes, can provide many advantages: easy separation from reaction mixture by filtration, without rinsing, easy regeneration and less corrosion, which makes them suitable for safe, inexpensive and eco-friendly production of biodiesel [3,53,60]. In addition, heterogeneous catalysts can simultaneously catalyze transesterification and esterification, thus avoiding the preesterification step. Therefore, heterogeneous catalysts are particularly useful for the processes with raw materials that have a high content of FFA. However, heterogeneous synthesis of biodiesel takes place much more slowly than the homogeneous

one, because the reaction mixture is a three-phase system in which mass transfer diffusion usually limits the overall reaction rate [3].

3.2.1. Acid catalysis

Having a variety of acid sites with different strength acidity, solid acid catalysts are used in many industrial processes despite the lower catalytic activity, compared to strong liquid acids [61]. Solid acid catalysts replace strong liquid acids, eliminating corrosion problems and the wastewater treatment [50]. There are some difficulties in using acid solid catalysts in biodiesel production. The factors affecting solid catalyst activity, such as acid strength are not clearly formulated and fully understood. In addition, it is not yet routinely possible to obtain porous solid catalysts with uniform size or geometry of the pores [62].

Only Kelkar et al. [36] used ultrasonic cavitation for intensification of esterification of C_8-C_{10} fatty acid odor cut, a WCO, with methanol catalyzed with superacid clay (chlorosulfonic acid supported on zirconium) in powder form (Table 1). At 1% of catalyst loading, the extent of conversion was about 75 mol% in 5 h of reaction time, with intermittent regeneration of catalyst after 150 min of reaction time. The catalyst gets deactivated during the reaction probably because of the water adsorption on the active sites of the catalyst and cannot be effectively recycled. However, at 2% of catalyst, 97% conversion was achieved in 7 h without substantial deactivation of the catalyst. Compared to the homogeneous process, the use of solid catalyst significantly slows down the process (Table 1), and the catalyst could not be effectively recycled after use (recycled catalyst gave only 41% conversion).

3.2.2. Base catalysis

Base solid catalysts have been used in several studies on low-frequency UA methanolysis of various oils (palm, rapeseed and *Jatropha* oil and waste soybean oil) in batch reactors, as can be seen in Table 4. These catalysts include CaO [63,64], SrO and BaO [63,65], Mg MCM-41, Mg-Al hydrotalcite, K+ impregnated zirconia [53,55], Ca–Mg–Al [66] or Zn–Mg–Al [58] hydrotalcite, Na/SiO_2 [18], KF/CaO [67] and $KF/\gamma\text{-}Al_2O_3$ [68]. The activity of base solid catalysts is related to their basic strength, so that the most basic catalyst showed the highest conversion. For instance, the activities of the alkaline earth metal oxides increased according to their basicity, i.e. CaO < SrO < BaO, opposite to their total surface areas [63]. Also, Mg–Al hydrotalcite, the most basic catalyst among four base solid catalysts used by Georgogianni et al. [53,55], showed the highest activity. The wave amplitude and sonication time in pulse mode, i.e. the ultrasonic energy dissipated appears to affect the biodiesel yield [18,42,65,68]. It seems that the optimum specific ultrasonic energy dissipated into the reaction system exists. Ren et al. [68] have recently shown that in the range of specific ultrasonic energy between 26.7 and 66.7 W/dm^3 the highest biodiesel yield of 98.7% is obtained at 53.3 W/dm^3. Two possible sources cause the loss of efficiency in the ultrasonic energy transfer through the liquids at larger energies than the optimum: the coalescence of small cavitation bubbles into larger ones which act as a barrier to that transfer and the decoupling effect [18,69]. The wave frequency and specific ultrasonic energy influence the biodiesel yield in the continuous sonication mode. Qian et al. [67] have recently shown in the range between 20 and 48 kHz that the smaller the frequency the higher the biodiesel yield and the initial reaction rate are as well as that the biodiesel yield increases with increasing the ultrasonic intensity up to 1.01 W/cm^2.

The use of solid base catalysts does not lead to soap formation. However, they are much less efficient in accelerating the methanolysis of rapeseed oil than a homogeneous base catalyst (sodium hydroxide), both in the presence and the absence of LFU [53], which can be attributed to the mass transfer limitations caused by the presence of solid particles in the liquid-liquid system. Under optimum conditions, the most effective base solid catalysts, BaO and Ca–Mg–Al hydrotalcite, ensure yields of biodiesel from palm and *Jatropha* oils about 95% in 50–60 min [63,65] and 30 min [66], respectively. Ca–Mg–Al hydrotalcite could be reused twelve times after washing of the adsorbed glycerol from the surface of catalyst with ethanol [66].

Alcohol-to-oil molar ratio has a large effect on solid base catalyzed transesterification under ultrasound irradiation. Kumar et al. [18] reported that the yield of methyl esters reaches the maximum of about 98% at the 9/1 methanol-to-*Jatropha* oil molar ratio, after which it remains constant.

3.3. Enzyme-catalyzed transesterification[1]

So far, little research has been done on the use of ultrasound irradiation in enzyme-catalyzed biodiesel production, as can be seen in Table 5. Only Novozym 435, a commercial lipase preparation from *Candida antarctica*, has been tested in the studies on UA transesterification reactions of soybean and high acid value waste oil with methanol and propanol, respectively. Enzyme activity of Novozym 435 in transesterification reactions is enhanced by ultrasound irradiation [30,70–72]. Ultrasonic irradiation ensures the same yields of FAME as vibration mixing in relatively shorter time [72]. Biodiesel production rate is further enhanced by combining ultrasonic and vibration mixing and a 96% yield of FAME could be achieved under the optimum conditions in 4 h, with no obvious loss in lipase activity after repeated use for five cycles. The presence of tert-amyl alcohol improved the solubility of methanol in the reaction mixture eliminating the inhibitory effects of methanol [72].

Wang et al. [30] optimized UA enzyme-catalyzed biodiesel production from high acid value waste oil and 1-propanol by esterification and transesterification with respect to the amount of lipases, propanol-to-oil molar ratio, and frequency and power of ultrasound. Immobilized lipase Novozym 435 was utilized as a biocatalyst. Under optimal conditions, such as 8% oil quantity of Novozym 435, the propanol-to-oil molar ratio of 3/1, the frequency and power of ultrasound of 28 kHz and 100 W, and the temperature of 40–45 °C, the conversion degree of 94.86% to propyl oleate was achieved in 50 min. Also, it was noticed that short-chain linear and branched alcohols (C_1–C_5) showed high conversion to FAAE [30].

4. Comparing different techniques for biodiesel production

Several studies deal with comparison of UA transesterification reactions with other techniques for biodiesel production such as mechanical stirring combined with heating, microwave irradiation and hydrodynamic cavitation, and they are reviewed in Table 6.

Compared to the systems with mechanical agitation and heating, biodiesel yields are generally higher under ultrasound irradiation and are achieved in shorter reaction times independently of type of sonication, catalyst and feedstocks, although there is disagreement among the researchers. Santos et al. [32] compared the effect of ultrasound in the sulfuric acid-catalyzed esterification of *O. niloticus* oil at the optimal operating condition. The ultrasonic process presented a lower initial reaction rate but after 10 min of reaction the yield of methyl esters became higher (98.2%), compared to 85% yield under mechanical stirring

[1] Enzymes are large-molecular-weight proteins of colloidal size, 10–100 nm, so enzyme reaction systems represent a gray region between homogeneous and heterogeneous ones, and therefore enzyme-catalyzed transesterification reactions are separately discussed.

Table 4
UA heterogeneous base-catalyzed methanolysis of various oils: direct sonication (horn).

Frequency/power	Feedstock	Alcohol	Alcohol-to-oil molar ratio (mol/mol)	Temperature (°C)	Catalyst/loading (wt%)	Yield (%)/time (min)	Optimal reaction conditions		Reference
							Operation conditions	Yield (%)/time (min)	
35 kHz	Sunflower oil	Methanol	4/1	40–75	CaO solid (thermal activation) CaO microcrystalline (ultrasonic activation)	80/45 92/120			[64]
24 kHz, 200 W	Rapeseed oil	Methanol	7/1	60	Mg/MCM-41/10 Mg–Al Hydrotalcite/10 10 K/ZrO_2/10 20 K/ZrO_2/20	89/300 96/300 70/300 83/300	–	–	[53]
24 kHz, 200 W	Waste soybean oil	Methanol	7/1	60	Mg/MCM-41/10 Mg–Al Hydrotalcite/10 10 K/ZrO_2/10 20 K/ZrO_2/20	22–89/60–300 29–96/60–300 28–70/60–300 33–83/60–300	–	–	[55]
20 kHz, 210 W	Jatropha oil	Methanol	–	–	Ca–Mg–Al/–	–	4/1,1.5%, 60 °C	94.3/30	[66]
20 kHz, 200 W	Palm oil	Methanol	3/1,6/1, 9/1,12/1, 15/1	65 ± 2	CaO SrO BaO/ 0.5–3.0	5.5–77.3/60 48.2–95.2/60 67.3–95.2/60	12/1 3%, 50% 9/1 amplitude 9/1	95/60	[63]
20 kHz, 200 W	Palm oil	Methanol	3/1,6/1, 9/1,12/1, 15/1	65 ± 2	SrO/0.5–3.0 BaO/0.5–3.0	40.68–95.17/60	9/1, 2.8% cat amplitude~80 amplitude~70	>95/50 >95/50	[65]
24 kHz, 200 W Amplitude 30–70%; Pulse mode 0.3–0.9 s/s	Jatropha oil	Methanol	5/1,7/1,9/1, 11/1,13/1,	–	Na/SiO_2/1, 2, 3, 4, 5		9/1, 3%, 50% amplitude, 0.7 s/s	98.53/15	[18]
20, 28, 40 kHz, 0.1–1.01 W/cm^2		Methanol	3/1,6/1,9/1 12/1,15/1,18/1	45–75	KF/CaO/1, 2, 3, 4, 5		12/1, 3%, 65 °C	99.6/60	[67]
26.7–66.7 W/dm^3	Soybean oil	Methanol	3/1,6/1,9/1 12/1,15/1	25–65	KF/γ-Al_2O_3/1, 2, 3, 4, 5		6/1, 35, 45 °C 53.3 W/dm^3	98.7/35	[68]

Table 5
A review on the applications of ultrasound irradiation in lipase-catalyzed biodiesel production: indirect sonication (ultrasonic cleaning bath).

Frequency/power	Feedstock	Alcohol	Alcohol-to-oil molar ratio (mol/mol)	Temperature (°C)	Biocatalyst/loading (wt%)	Yield (%)/time (min)	Optimal reaction conditions		Notification	Reference
							Operation conditions	Yield (%)/time (min)		
40 kHz/500 W	Soybean oil	Methanol	1/1–36/1	40	Novozym 435[a]/6	93/720	Novozym 435/6, 6/1 methano/oil 1/1 tert amyl alc/oil (vol), 50% power, 50 rpm vibration	96/240	Slight decrease in enzyme activity (4%) after 5 uses	[72]
40 kHz/500 W + 50 rpm vibration						96/240				
28 kHz/100 W	High acid value waste oil	Propanol		40–45	Novozym 435		3/1, Novozym 435/8	94.86/50	High conversion ratio of linear and branch alcohols (C_1–C_5)	[30]

[a] *Candida antarctica* lipase B immobilized on polyacrylic resin.

process. On the other side, conversions did not differ greatly in the p-toluenesulfonic acid-catalyzed methanolysis of rapeseed oil under ultrasonic and mechanical mixing [13]. Similarly, comparing base-catalyzed methanolysis of vegetable oils [10,11,54], beef tallow [33] and WCO [27,29] in the presence of LFU and mechanical agitation showed that ultrasonic irradiation ensured a shorter reaction time. However, Lifka and Ondruschka [13] and Georgogianni et al. [53] observed no significant influence of the mixing method (ultrasonic versus mechanical agitation) on the reaction rate and the biodiesel yield in the sodium hydroxide-catalyzed methanolysis of rapeseed oil. This discrepancy is attributed to different types of ultrasonic reactors and reaction conditions applied [73]. The heterogeneous base-catalyzed methanolysis reactions in the presence of ultrasound are significantly faster than those carried out using mechanical stirring under the same reaction conditions (Georgogianni et al. [18,53,63,67]). This might be partly due to some physical changes on the surface texture of the solid catalysts caused by ultrasound, which generate new catalytically active surface area and contribute to the catalytic activity in the long run [63].

Microwave irradiation is another alternative efficient heating method used to shorten the transesterification over the past few years. The microwave irradiation potential to be an efficient and cost-competitive technique for large-scale biodiesel production is nowadays well-recognized. Its advantages are a drastic reduction in the quantity of by-products and a short separation time [74]. Refaat and El Sheltawy [29] conducted base-catalyzed biodiesel production from waste vegetable oil under mechanical mixing, LFU and the microwave irradiation. Application of radio frequency microwave gave 100% yield in 2 min, compared to ~99% yield obtained in 5 min using ultrasonic mixing, while the static separation time was 25 min in both cases [29]. The transesterification, even at a low solid catalyst loading, was complete in 30 min due to the thermal effects [22]. No leaching problem was observed with microwave irradiation, unlike ultrasound irradiation, even with high solid catalyst loadings. Hsiao et al. [75] reported new method for transesterification of soybean oil to produce biodiesel that combined ultrasonic mixing and closed microwave irradiation. The optimal method that gave 97.7% conversion involved 1-min ultrasonic mixing followed by 2-min closed microwave irradiation and 1.0 wt% of used catalyst; reaction temperature of 60 °C and 6/1 methanol-to-oil molar ratio. The new method was more efficient than both ultrasound and closed microwave irradiation giving 90.2% and 21% conversion, respectively, in 10 min.

Hydrodynamic cavitation is also a potential method for large-scale biodiesel production because of its easy scale-up. Cavitation events identical to acoustic cavitation are generated in hydrodynamic cavitation when a liquid flows, for instance, through orifice plates. The liquid flashes, generating many cavities when the pressure at orifices falls below the vapor pressure of that liquid. The transesterification reaction of soybean, castor and peanut oils using sodium hydroxide and methanol was studied in the presence of hydrodynamic cavitation [12,16]. Depending on the vegetable oil, biodiesel yields in the range between 90 and 99% are obtained in 10–15 min of the reaction time [16]. Comparing base-catalyzed biodiesel production using mechanical stirring, ultrasonic and hydrodynamic cavitation, Ji et al. [12] established that both power ultrasonic and hydrodynamic cavitation gave shorter reaction time (10–30 min) than mechanical stirring. Kelkar et al. [36] investigated esterification of C_8–C_{10} fatty acid cut with methanol, using concentrated H_2SO_4 under hydrodynamic and ultrasonic cavitation and reported 92% and 95% conversion in only 90 min, respectively. A careful design of the hydrodynamic systems allows gaining conditions similar to those during acoustic cavitation, but at lower energy inputs as compared to ultrasonic reactors [12,36,76].

Table 6
Comparing different methods for biodiesel production.

Method	Vegetable oil, alcohol, reaction conditions	Ultrasound assisted alcoholysis		Other methods		Reference
		Sonication conditions	Yield/time %/min	Operating conditions	Yield/time %/min	
Homogeneous, acid-catalyzed	Oleic acid, ethanol, 3/1; 5% H_2SO_4; 60 °C	Bath, 40 kHz, total power 1200 W	95/120	Mechanical stirring	86/300	[35]
	FFA from *Oreochromis niloticus*, methanol, 9/1, 2% H_2SO_4, 30 °C	Bath, 40 kHz, total power 60 W	98.2/90	Mechanical stirring	85/90	[32]
	Rapeseed oil, methanol, 3.3/1, 3.75% p-toluenesulfonic acid, 45 °C	Horn, 20% (4 W)	11.6/180	Mechanical stirring (ultra-turrax)	11.0/180	[13]
	C_8–C_{10} fatty acid cut, methanol, 10/1, 1% H_2SO_4; 28 °C	Bath, 20 kHz, total power 120 W	98/120	Hydrodynamic cavitation	92/90	[36]
Homogeneous, base-catalyzed	Soybean oil, methanol, 6/1, 1.0% KOH,	Horn, 20 kHz, total power 150 W	99/10	Mechanical stirring	97/60	[12]
				Hydrodynamic cavitation	99/30	
	Vegetable oils, 4/4 (w/v), 0.5, 1.0% NaOH, na	Bath, 20 kHz, total power 85 W		Hydrodynamic cavitation		[16]
	Soybean oil		97/15		98/15	
	Castor oil		99/10		99/10	
	Peanut oil		99/10		90/10	
	Soybean oil, methanol, 5/1, approx. 1% NaOH, 60 °C	Horn, 20 kHz, total power 2200 W	96/1.5 (pulse mode) 86/0.25(cont. mode)	Mechanical stirring	96/45	[11]
	Rapeseed oil, methanol, 7/1, 2% NaOH, 60 °C	Horn, 24 kHz, total power 200 W	96/20	Mechanical stirring	96/20	[53]
	Rapeseed oil, methanol, 3.3/1, 0.5% NaOH, 45 °C	Horn, 20% (4 W)	80/20	Mechanical stirring (ultra-turrax)	85/20	[13]
	Soybean oil, methanol, 6/1, 1% NaOH, 30 °C	Horn, 20, kHz, total power 600 W	90.2/10	Microwave irradiation	21/10	[75]
	Beef tallow, methanol, 6/1, 0.5% KOH, 60 °C	Horn, 20 kHz, total power 400 W	92/1.17	Mechanical stirring	91/60	[33]
	Waste vegetable oil, methanol, 6/1; 1% KOH, 65 °C	Horn, 20 kHz, total power 100 W	98.94/5	Mechanical stirring	96.15/60	[29]
				Microwave irradiation	100/2	
	Triolein, various alcohols, 6/1; 1% KOH; 25 °C	Bath, 40 kHz, total power 1200 W	92/15[a]	Mechanical stirring	77/25[a]	[39]
	Waste cooking oil, methanol, 6/1, 0.5–1.5% KOH, 30 °C	US homogenizer, 20 kHz, output power 400 W	96.78/30	Mechanical stirring	90/60 (60 °C)	[27]
Heterogeneous, base-catalyzed	Jatropha curcus oil, methanol, 9/1; 3% $NaSiO_2$, ambient temperature	Horn, 24 kHz, total power 200 W	~99/15	Mechanical stirring	~99/360	[18]
	Rapeseed oil, methanol, 7/1, 10, 20%, 60 °C					[53]
	Mg/MCM-41/10	Horn, 24 kHz, total power 200 W	89/300	Mechanical stirring	85/24 × 60	
	Mg–Al Hydrotalcite/10		96/300		97/24 × 60	
	10 K/ZrO_2/10		70/300		67/24 × 60	
	20 K/ZrO_2/20		83/300		89/24 × 60	
	Oil, methanol, 12/1, 3% KF/CaO, 65 °C	20 kHz	98.7/60	Mechanical stirring	90/150	[67]
	Palm oil, methanol, 12/1, 3% CaO, 65 °C		77.3/60		5.5/60	[63]
	9/1, 3% SrO, 65 °C	Horn, 20 kHz, total power 200 W	95.2/60	Mechanical stirring	48.2/60	
	9/1, 3% BaO, 65 °C		95.2/60		67.3/60	

[a] For isopropyl alcohol Mixsonix Sonicator 3000.

5. Possibilities for improvement of ultrasound-assisted biodiesel production

While transesterification is well-established and becoming increasingly important, there remain considerable inefficiencies in existing processes. Therefore, there is an imperative need to develop an efficient, time-saving, economically functional and environmental friendly large-scale biodiesel production process superior to the existing methods. UA transesterification is among these alternative and innovative biodiesel production processes. The use of ultrasound has been already shown to be very effective for intensification of biodiesel production processes. Despite the large potential for UA transesterification, further studies are needed to overcome considerable technical and process limitations. Several different approaches have been used in the last decade to improve the UA biodiesel production such as the optimization of process factors using statistical methods, modeling the process kinetics, the application of *in situ* UA transesterification processes, the use of phase transfer catalysts, the use of a continuous process instead of batch ones and the development and application of novel types of ultrasonic reactors.

5.1. Optimization using statistical methods

Usually, a set of optimal levels of the important operational factors maximizes the biodiesel yield. Optimizing each factor individually, i.e. changing one factor at a time while others are kept unchanged is time consuming and the reached optimum is never true because the interaction among variables cannot be taken into consideration. However, a transesterification process can be optimized more effectively by using mathematical (statistical) methods known as experimental design. By varying the analyzed factors

simultaneously, one gets more complete information on the studied process with a minimal number of experiments and the lowest possible material costs. This approach leads not only to a better understanding and knowledge of the process but also to the optimum process conditions maximizing the biodiesel yield. The mathematical model coming out from the optimization study should be validated and proven to be statistically adequate and accurate to predict the maximum biodiesel yield. Afterwards, the model can be used for scale-up and commercialization of biodiesel production processes.

The base-catalyzed transesterification of different feedstocks in the absence of ultrasound has been frequently optimized by using the design of experiments. However, a few studies have been dealt with the optimization of low-frequency UA methanolysis to produce biodiesel from soybean [12,19], palm [65] sunflower [73] and crude cottonseed [77] oils. Kelkar et al. [36] and Santos et al. [32] optimized the acid-catalyzed methanolysis of fatty acid odor cut (C_8–C_{10}) and *O. niloticus* oils, respectively, under LFU irradiation. In these studies, the influence of the operating factors on the FAME yield has been evaluated using statistical analysis methods such as orthogonality analysis [12] and response surface methodology based on central composite rotatable design [19,65,77], and full factorial experiment 3^3 with replication [73]. Only Mahamuni and Adewuyi [46,47] studied optimization of the base-catalyzed methanolysis of soybean oil in the presence of high-frequency ultrasound. Application of Taguchi method enabled optimization of this ultrasonically assisted batch transesterification process using very few experiments [47]. The optimum conditions: 581 kHz, 143 W, 0.75% (w/w) KOH loading and 6/1 methanol-to-oil molar ratio resulted in more than 92.5% biodiesel yield in less than 30 min.

Ji et al. [12] reported the order of the effect of the operating factors on FAME yield in the sodium hydroxide catalyzed methanolysis of soybean oil as follows: methanol-to-oil molar ratio > temperature > pulse frequency > ultrasonic power, while the catalyst loading was not optimized. Santos et al. [19] optimized the production of FAME from soybean oil by low-frequency high-intensity UA methanolysis, regarding methanol-to-oil molar ratio and catalyst loading. Using low base catalyst loadings (0.2–0.6%) at 29 °C, the methanol-to-oil molar ratio mostly influenced FAME yield, while the catalyst loading showed low significance with observation that the excess catalyst negatively affected FAME yield. Fan et al. [77] optimized the three reaction variables – methanol-to-oil molar ratio, catalyst (sodium hydroxide) concentration and reaction time for transesterification of crude cottonseed oil at 25 °C under 40 kHz ultrasonic irradiation. The methyl ester yield of 98% could be reached at the following optimal conditions: methanol-to-oil molar ratio of 6.2/1, sodium hydroxide concentration of 1% (by the weight of oil) and reaction time of 8 min [77]. Avramović et al. [73] established that all three reaction variables, the methanol-to-oil molar ratio, the potassium hydroxide catalyst loading and the reaction temperature as well as the interaction of the reaction temperature and the methanol-to-oil molar ratio were effective on fatty acid methyl ester formation at the 95% confidence level, the most important factor being the catalyst loading. The relationship between the factors and their interactions were modeled by the second-order polynomial equation. The highest FAME yield of 88.0% obtained in 60 min under the optimum reaction conditions according to second order polynomial model: temperature of 32.2 °C, methanol-to-oil molar ratio of 7.5/1 and catalyst loading of 0.7.

For the production of FAME from *O. niloticus* oil by low-frequency high-intensity ultrasound assisted acid catalyzed methanolysis, the most important factor affecting the yield is the alcohol-to-FFA molar ratio [32]. The highest yield observed is 98.2% after 90 min of reaction under the next set of the optimal operating condition: alcohol-to-oil molar ratio of 9.0/1, catalyst (sulfuric acid) loading of 2.0% (w/w) and temperature of 30 °C. Kelkar et al. [36] optimized acid catalyzed esterification of C_8–C_{10} fatty acid cut with methanol under hydrodynamic and ultrasonic cavitation. The optimal operating condition being 10/1 alcohol-to-fatty acid molar ratio, 2% (w/w) of conc. sulfuric acid catalyst loading, resulted in >95% conversion in 90 min of processing time.

Salamatinia et al. [65] statistically evaluated the UA heterogeneous biodiesel production from palm oil using BaO and SrO as catalysts. Four different variables: reaction time (10–60 min), alcohol-to-oil molar ratio (3/1 to 15/1), catalyst loading (0.5–3.0 wt%) and ultrasonic amplitude (25–100%) were optimized. The optimum conditions for the ultrasonic-assisted biodiesel production process: the reaction time of nearly 50 min, the methanol-to-oil molar ratio of 9/1 and the catalyst loading of merely 3% and ultrasonic amplitudes of ~70 and ~80% for the BaO and SrO catalysts, respectively, gave biodiesel yields of above 94%.

5.2. Modeling the kinetics of transesterification processes

Transesterification reaction kinetics is essential for biodiesel production process development which provides valuable data for reactor design, operation and scale-up, process analysis, simulation and optimization, process control, evaluation of the industrial feasibility of new processes, catalyst development, etc. A thorough and quantitative knowledge of the transesterification reaction kinetics is required to reach the above objectives through kinetic modeling, which is aimed toward deriving mathematical models that describe the rate of transesterification reaction. Knowing kinetic model helps one to predict the transesterification reaction rate and the biodiesel yield under the certain reaction conditions (alcohol-to-oil molar ratio, catalyst loading and temperature). However, other factors than kinetics such as mixing and reactor fluid-dynamics can also affect the reaction rate. The choice of proper kinetic and flow models is critical for accurate modeling the effects of process operating conditions.

Since ultrasound has only physical effects, it can be expected that the same kinetic models are acceptable for the reaction carried out in both the presence and the absence of ultrasound irradiation. Therefore, the kinetic models for the transesterification reaction in the absence of ultrasound are shortly reviewed. The kinetics of the homogeneous base-catalyzed transesterification reaction has been most frequently studied using either rigorous [40,78–80] or empirical [23,24,48,81,82] kinetic models. The former are based on the reaction mechanism consisting of three reversible consecutive-competitive reactions and have the advantage related to their prediction accuracy over a wide operating range. The latter assume the irreversible overall reaction, have the rate constant determined strictly by fitting to experimental data and allow simple computation. Also, a heterogeneous stage controlled by the mass transfer rate is shown in the beginning of the methanolysis reaction, which has been included in the overall process kinetic model only in a study [82]. For the heterogeneously catalyzed methanolysis reaction different empirical kinetic models have been developed. The kinetics of metal oxide catalyzed soybean oil methanolysis at high temperatures was described by a simple first-order kinetic model with respect to TAG [83] or methanol [84]. The order of the CaO- and $Ca(OH)_2$-catalyzed methanolysis with respect to TAG changed from zero to one with the reaction progress [85]. However, it has been shown that the kinetic model of CaO- and $Ca(OH)_2$-catalyzed methanolysis includes the initial mass transfer controlled regime followed by the pseudo-first order reaction controlled regime [86,87]. Lipase transesterification of TAG involves a two-step mechanism when looking at a single ester bond: hydrolysis of the ester bond and release of the alcohol moiety followed by an esterification with the second substrate. This mechanism conforming to a Ping Pong Bi Bi mechanism is the widely accepted mechanism for

transesterification of TAG [88,89], although the Michaelis–Menten kinetics is applied when fitting to experimental data [90,91].

The kinetics of UA methanolysis has hardly been studied, and contradictory results have been reported. Deshmane et al. [92] verified a kinetic model based on the first order reaction followed by the second order with respect to fatty acids for the UA acid-catalyzed esterification of palm fatty acid distillate. Georgogianni et al. [23,24] reported the first and second order reaction with respect to TAG for the base-catalyzed methanolysis of sunflower and cottonseed oils, using both LFU and mechanical agitation, although a better fit was obtained for the first order reaction kinetics [23,24]. However, Colucci et al. [48] and Avramović [49] established a pseudo second-order kinetic model with respect to TAG for the base-catalyzed methanolysis of soybean and sunflower oil, respectively. The kinetic model is actually the same as that for the base-catalyzed methanolysis in the absence of ultrasound, indicating that the same phenomena control the process rate independently of the type of mixing applied [73]. The initial mass transfer controlled regime exists in the beginning of the reaction, but it has been not included in modeling yet [73].

Stavarache et al. [45] observed that the amount of DAG, the first intermediate in the stepwise transesterification mechanism, unlike their expected accumulation, was low from the beginning of the reaction, and decreased as the reaction advanced, reaching a constant value after 30 min. They concluded the rate-determining reaction switches from the conversion of DAG to MAG in the agitated reactor to the conversion of MAG to FAAE and glycerol under ultrasonic irradiation. The FAME formed under ultrasonic irradiation were identical to those formed in the stirred reactor [44].

5.3. In situ ultrasound-assisted biodiesel production

The *in situ* biodiesel production is a novel approach for producing biodiesel from oil bearing materials such as oilseeds or seed cakes and acidified or alkalized alcohol, developed by Harrington and D'Arcy-Evans [93]. In this method, the alcohol acts as an extracting solvent and an esterification reagent, so both oil extraction and transesterification reaction proceed in one step. Usually, the oil bearing material is directly treated at ambient temperature and pressure with an alcohol solution of the catalyst. The method eliminates the need for the isolation and possibly refining of seed oils, so the biodiesel production process could reduce costs and maximize the product yield. When applying indirect ultrasound for the *in situ* biodiesel production it is preferable to use additional mechanical stirring, which provides enough mixing for the maximum exposure of the reactant to the reaction medium during sonication [26].

This method has been carried out both in the absence and the presence of ultrasound irradiation. A review of UA *in situ* biodiesel production is given in Table 7. The use of ultrasound in the biodiesel production from seed cakes by base-catalyzed methanolysis reaction shortens reaction time and enhances total FAME yields under milder reaction conditions, compared to the conventional method [25]. The total FAME yields from cotton, sunflower and sesame seeds are increased from 46 to 85.5%, 67.2 to 93%, and 43.2 to 83.5%, respectively. *In situ* methanolysis of cotton [23] and sunflower [24] seeds produces FAME in yields significantly greater than those obtained from the conventional reaction with pre-extracted seed oils. The base-catalyzed *in situ* methanolysis and ethanolysis require only 20 and 40 min, respectively, for complete conversion using ultrasonication. The respective time for the conventional *in situ* base-catalyzed methanolysis was 1 h while ethanolysis transesterification reaction was not completed even after 4 h. Generally, UA methanolysis gives high yields of methyl esters (95%) after a short reaction time (20 min), while the

Table 7
A review on the UA *in situ* transesterification of different feedstocks: indirect sonication.

Frequency/power[a]	Feedstock	Alcohol	Alcohol-to-oil molar ratio (mol/mol)	Temperature (°C)	Catalyst/loading (wt%)	Yield (%)/time (min)	Optimal reaction conditions		Reference
							Operation conditions	Yield (%)/time (min)	
35 kHz, na	*Cynara cardulus* seeds	n-Hexan Methanol	1/1, 25/1	25	NaOH/0.2–1.2	78.5/30	–	–	[25]
	Cotton:								
	Seeds					40/30			
	Cakes					76.9/30			
	Sunflower:								
	Seeds					43.7/30			
	Cakes					83.5/30			
	Sesame:								
	Seeds					61.7/30			
	Cakes					77.2/30			
24 kHz, 200 W	Sunflower seeds	Methanol	7/1	60	NaOH/	88–97/10–40	2% NaOH	95/20	[24]
		Ethanol		80	1.0, 1.5, 2.0	78–98/20–40		98/40	
24 kHz, 200 W	Cottonseed	Methanol	7/1	60	NaOH/	86–97/10–40	2% NaOH	97/40	[23]
		Ethanol		80	1.0, 1.5, 2.0	78–98/20–40		98/40	
35 kHz, 500 W	Rice bran	Methanol	10/1	60 ± 2	H_2SO_4/27.6	82.79/240 (medium FFA content of 47.87%) 79.08/240 (low FFA content of 13.27%)	–	–	[26]

[a] Ultrasonic cleaning bath.

ethanolysis gives yields significantly lower than those obtained by the methanolysis. Ultrasound is also effective in increasing the FAME yield in the acid-catalyzed *in situ* production of biodiesel from rice bran with low FFA content [26].

5.4. Phase transfer catalysis

As already emphasized, immiscibility of alcohol and oils is a critical factor affecting the rate of transesterification reaction in its initial heterogeneous stage. There are several approaches to overcome the mass transfer limitation such as the use of efficient mixing, inert co-solvents, supercritical conditions and phase transfer catalysts (PTC). The mass transfer limitation is eliminated by disintegrating the dispersed alcohol into small stable drops, by forming a pseudo-single phase, by dissolving alcohol into the oil phase and facilitating the interphase transfer of reactants, respectively. The processes based on the use of PTC are known as phase transfer catalysis.

Most commonly used PTC are onium salts (ammonium and phosphonium salts), macrocyclic polyethers (crown ethers) and aza-macrobicyclic ethers (cryptands). The soap formed in the saponification reaction is also claimed to act as PTC for base-catalyzed methanolysis of vegetable oils [10]. No need for expensive aprotic solvents, simpler scale-up and shorter reaction time are advantages of reactions in the presence of PTC over the conventional methods [94]. PTC accumulates at the interface and produces an emulsion with smaller droplet size, which has a higher surface area for reaction [95]. By facilitating the interphase transfer of reactants, PTC makes the reaction between two immiscible reactants possible. The activity of a PTC depends on its cation and anion [94]. A combination of PTC catalyst which initiates the reaction by the transfer of reactants across the interfacial area and ultrasound which enhances the mass transfer trough increasing the interfacial area is better than either of the two techniques alone [96]. Zhang et al. [94] investigated the possibility of enhancing the base-catalyzed transesterification of soybean oil in the presence of different ammonium type of PTC combined with LFU (20 kHz). Generally, FAME yield increases with increasing methanol-to-oil and total OH^--to-oil molar ratios both in the presence and the absence of ultrasound. A higher final FAME yield was obtained with ultrasound, compared to that with a magnetic stirrer.

5.5. Continuous ultrasound-assisted biodiesel production

There are two basic procedures for biodiesel synthesis, batch and continuous, which can be carried out at room or higher temperatures, at the atmospheric or elevated pressure and in the presence or absence of appropriate catalysts [97]. In batch processes, the reaction and the separation stages are usually carried out in the same tank, so it requires greater volume of the reactor and longer reaction and separation times [60,97]. In addition, the batch procedure is inefficient due to its inert nature when starting and ending and the product quality varies from batch to batch, which increase labor costs. Continuous process improves the overall economic effect, providing a lower production cost, uniform product quality and easier control of the process and decreasing the reactor volume by reducing retention time required to achieve the desired degree of TAG conversion [97]. Continuous UA biodiesel synthesis is suitable for processing large amounts of vegetable oil in relatively small reactor volume [98]. Flow ultrasonic reactors stand out for greater efficiency and flexibility and lower energy consumption than batch ones [56]. A review of a few studies on continuous biodiesel production using ultrasound is given in Table 8.

Table 8
A review on the UA base-catalyzed continuous transesterification of different feedstocks: direct sonication.

Frequency/power	Feedstock	Alcohol	Reactor volume (L)	Residence time/(min)	Alcohol-to-oil molar ratio (mol/mol)	Temperature (°C)	Catalyst/loading (wt%)	Yield (%)/time (min)	Optimal reaction conditions		Reference
									Operation conditions	Yield (%)/time (min)	
45 kHz/600 W 100% power	Palm oil	Methanol	2.62	10, 20, 30	6/1	38–40	KOH/	96.25/10 97.5/20 91.25/30	–	–	[98]
	Commercial edible oil		(for 12 vol replacements) 6.35		7.5/1 7.5/1			94.5/10 93/20 95/30 50/30 <90/20			
20 kHz/1 kW	WCO	Methanol	0.8	1.6 0.32	2.5/1, 3/3, 3.5/1, 4/1 1/1, 1.5/1, 2/1	20–25	KOH/0.7 KOH/0.3	80.52–89.30 97.10–99.20	4/1 (2.5/1 + 1.5/1), 1% KOH (0.7 + 0.3), 0.93 min RT	93.8	[60]
20 kHz, 210 W ultrasonic tubular reactor	Jatropha oil	Methanol	–	–	–	60	–	–	4/1, 60 °C, 1.2% Zn–Mg–Al hydrotalcite	94.3	[58]

Only base-catalyzed methanolysis of edible oils and WCO are performed in continuous flow reactors. The FAME yield depends on the reactor size and the residence time [98]. Higher FAME yields (over 95%) are obtained in the smaller reactor (6.35 L) than in the larger one (2.62 L) in the range of the residence time 10–30 min. Only for the smaller reactor the highest residence time gives the lower FAME yields than shorter residence times. These results show that using a better design of the reactor with efficient mixing could shorten the reaction time and reduce the production costs, enabling the use of ultrasound for large scale processing of vegetable oils [45]. The two-step continuous base-catalyzed methanolysis of WCO under LFU was studied by Thanh et al. [60]. The FAME yields were about 81% and 99% for the first and second step, respectively, while under the optimal conditions the recovery of biodiesel from WCO was 93.8% (Table 8).

However, ultrasound does not always contribute to better results. In the case of base-catalyzed methanolysis of recycled oil carried out in a specially designed continuous helicoidal reactor [99], the ultrasound applied favored formation of soaps and gels, which made the glycerol separation more difficult.

5.6. Special ultrasonic reactors

The use of novel reactor types with better performances than currently used is among the developing methods leading to reduce the production cost. Therefore, recent studies have been focused on the design and optimization of ultrasonic reactors to improve their features and performances. A combination of ultrasound action and flow reactors is a promising way to design novel, more efficient ultrasonic reactors such as loop reactors, pipe reactors and reactors with modular units combined in series [100]. The main problem is related to homogeneity of ultrasonic field in reactors as cavitation events are mainly concentrated very close to the ultrasonic processing probe. It is well-known that the reactor geometry affects greatly the kinetics of the reaction carried out. With increasing the reactor volume the ultrasound power dissipated to the reaction mixture should be increased to hold the same specific power input, which requires several ultrasonic transducers. To achieve a uniform ultrasonic field and optimal microstreaming through the whole reactor volume, ultrasonic reactors of complicated design are often needed such as multistage reactor having a number of smaller ultrasonic units. For sure, further studies on linking the reactor characteristics with cavitation bubble dynamics and the rheology of the reaction mixture at different scale applications are needed. The future of ultrasonic reactors lies in the design of the multiple frequency multiple transducer based reactors operating in a continuous mode [21,56]. Since the operating costs of ultrasonic reactors are higher than those of conventional reactors, the advantages obtained for a specific application should be weighed against the higher processing costs. Operating factors should be optimized for obtaining overall benefits.

Cintas et al. [56] developed a new ultrasonic pilot stop-flow reactor that is claimed to be well suited for transesterification scale-up. The best observed power/conversion ratio that gives total conversion to FAME after 1 h flow is at 600 W. This new reactor was applied to the soybean oil methanolysis at an extremely low ratio of methanol and catalyst and moderate energy consumption. Further energy saving is achieved by a two-step process where conventional heating under mechanical stirring is followed by ultrasound irradiation. Thanh et al. [51] developed a pilot plant using ultrasound irradiation method for biodiesel production from canola oil in which the transesterification was carried out by a circulation process at room temperature. Optimal reaction conditions: methanol-to-oil molar ratio 5/1, 0.7 wt% KOH gave maximum FAME yield greater than 99% within the 50 min of reaction time.

6. Conclusions

In the present paper state-of-the art and perspectives of UA biodiesel production from different oil-bearing materials using acid, base and enzyme catalysts are discussed. The importance of ultrasound characteristics and other process variables for the biodiesel yield and the reaction rate is focused on. So far, performed studies on UA biodiesel production have shown that the ultrasound action is primarily based on the emulsification of the immiscible liquid reactants by microturbulence generated by radial motion of cavitation bubbles while its chemical effect might be ignored. In the presence of solid catalyst, ultrasound can activate the solid catalyst, dislodge the materials occupying the inactive sites and increase the surface area for a reaction, the mixing intensity and the mass transport rate. However, ultrasound irradiation may cause the leaching of some solid catalysts at high catalyst loadings.

Compared to other techniques, LFU is shown to be a valuable tool in biodiesel synthesis, regarding to short reaction time, low temperature, low quantity of catalysts and low quantity of methanol, which make this method efficient, time saving and economically functional. Generally, in homogeneous transesterification processes the maximum biodiesel yields higher than 90% are obtained under the optimum reaction conditions within 3–30 min. Solid catalysts are much less efficient in accelerating the transesterification processes than homogeneous catalysts, but its use significantly simplifies the process of separation and purification of the products, reduces environmental problems and allows the reuse of catalysts, providing a positive economic effect. In addition, acid solid catalysts can simultaneously catalyze esterification and transesterification reactions avoiding the pre-esterification step. Compared to the chemical methods, biodiesel synthesis catalyzed by enzymes (lipases) offers many advantages, such as high selectivity, less energy consumption, less side products and waste, avoiding soap formation and easy recovering of glycerol and catalysts. However, the cost of lipase is the major obstacle for the use of lipases in industrial biodiesel production.

Despite a large potential for UA transesterification, further studies are needed to overcome considerable technical and process limitations. In that sense, there is the imperative need not only to improve the existing UA biodiesel production processes but also to investigate alternative production processes. The novel process should be efficient, time-saving, economically functional, environmental friendly and superior to the existing methods at large-scale. Several different developing methods reducing the biodiesel production costs are being currently investigated, such as the optimization of process factors using statistical methods, the development of the process kinetic models, the *in situ* ultrasound application in transesterification, the use of phase transfer catalysts, the use of the continuous process and the design of novel types of ultrasonic reactors. In the future, the special attention should be paid to the use of novel ultrasonic reactor types with better performances than currently used. A combination of ultrasound action and flow reactors is a promising way to design novel, more efficient ultrasonic reactors. It is expected that the future of ultrasonic reactors lies in the design of the multiple frequency multiple transducer based reactors operating in a continuous mode. For sure, further studies on linking the reactor characteristics with cavitation bubble dynamics and the rheology of the reaction mixture at different scale applications are needed.

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References

[1] Antolin G, Tinaut FV, Briceno Y. Optimization of biodiesel production by sunflower oil transesterification. Bioresour Technol 2002;83:111–4.
[2] Lang X, Dalai AK, Bakhshi NN. Preparation and characterization of bio-diesels from various bio-oils. Bioresour Technol 2001;80:53–62.
[3] Leung DYC, Wu X, Leung MKH. A review on biodiesel production using catalyzed transesterification. Appl Energy 2010;87:1083–95.
[4] Canakci M, Van Gerpen J. Biodiesel production from oils and fats with high free fatty acids. Trans Am Soc Agric Eng 2001;44:1429–36.
[5] Ataya F, Dubé MA, Ternan M. Acid-catalyzed transesterification of canola oil to biodiesel fuel under single- and two-phase reaction conditions. Energy Fuels 2007;21:2450.
[6] Ataya F, Dubé MA, Ternan M. Variables affecting the mass transfer limitations in the biodiesel reaction. Energy Fuels 2008;22:679.
[7] Marchetti JM, Miguel VU, Errazu AF. Possible methods for biodiesel production. Renew Sustain Energy Rev 2007;11:1300–11.
[8] Gerpen VJ. Biodiesel processing and production. Fuel Process Technol 2005;86:1097–107.
[9] Stamenković OS, Lazić ML, Todorović ZB, Veljković VB, Skala DU. The effect of agitation intensity on alkali-catalyzed methanolysis of sunflower oil. Bioresour Technol 2007;98:2688–99.
[10] Stavarache C, Vinatoru M, Nishimura R, Maeda Y. Fatty acids methyl esters from vegetable oil by means of ultrasonic energy. Ultrason Sonochem 2005;12:367–72.
[11] Chand P, Chintareddy VR, Verkade JG, Grewell D. Enhancing biodiesel production from soybean oil using ultrasonics. Energy Fuels 2010;24:2010–5.
[12] Ji J, Wang J, Li Y, Yu Y, Xu Z. Preparation of biodiesel with the help of ultrasonic and hydrodynamic cavitation. Ultrasonics 2006;44:411–4.
[13] Lifka J, Ondruschka B. Influence of mass transfer on the production of biodiesel. Chem Eng Technol 2004;27:1156–9.
[14] Mason TJ, Lorimer JP. Applied sonochemistry: uses of power ultrasound in chemistry and processing. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co.; 2002.
[15] Adewuyi YG. Sonochemistry: environmental science and engineering applications. Ind Eng Chem Res 2001;40:4681–715.
[16] Gogate PR, Tayal RK, Pandit AB. Cavitation: a technology on the horizon. Curr Sci 2006;91:35–46.
[17] Singh AK, Fernando SD, Hernandez R. Base-catalyzed fast transesterification of soybean oil using ultrasonication. Energy Fuels 2007;21:1161–4.
[18] Kumar D, Kumar G, Poonam CP, Singh. Ultrasonic-assisted transesterification of *Jatropha curcus* oil using solid catalyst, Na/SiO_2. Ultrason Sonochem 2010;17:839–44.
[19] Santos FFP, Rodrigues S, Fernandes FAN. Optimization of the production of biodiesel from soybean oil by ultrasound assisted methanolysis. Fuel Process Technol 2009;90:312–6.
[20] Kalva A, Sivasankar T, Moholkar VS. Physical mechanism of ultrasound-assisted synthesis of biodiesel. Ind Eng Chem Res 2009;48:534–44.
[21] Gogate PR. Cavitational reactors for process intensification of chemical processing applications: a critical review. Chem Eng Process 2008;47:515–27.
[22] Verziu M, Florea M, Simon S, Simon V, Filip P, Parvulescu V, et al. Transesterification of vegetable oils on basic large mesoporous alumina supported alkaline fluorides—evidences of the nature of the active site and catalytic performances. J Catal 2009;263:56–66.
[23] Georgogianni KG, Kontominas MG, Pomonis PJ, Avlonitis D, Gergis V. Alkaline conventional and in situ transesterification of cottonseed oil for the production of biodiesel. Energy Fuels 2008;22:2110–5.
[24] Georgogianni KG, Kontominas MG, Pomonis PJ, Avlonitis D, Gergis V. Conventional and in situ transesterification of sunflower seed oil for the production of biodiesel. Fuel Process Technol 2008;89:503–9.
[25] Siatis NG, Kimbaris AC, Pappas CS, Tarantilis PA, Polissiou MG. Improvement of biodiesel production based on the application of ultrasound: monitoring of the procedure by FTIR spectroscopy. J Am Oil Chem Soc 2006;83:53–7.
[26] Yustianingsih L, Zullaikah S, Ju Y-H. Ultrasound assisted in situ production of biodiesel from rice bran. J Energy Inst 2009;82:133–7.
[27] Babajide O, Petrik L, Amigun B, Ameer F. Low-cost feedstock conversion to biodiesel via ultrasound technology. Energies 2010;3:1691–703.
[28] Hingu SM, Gogate PR, Rathod VK. Synthesis of biodiesel from waste cooking oil using sonochemical reactors. Ultrason Sonochem 2010;17:827–32.
[29] Refaat AA, El Sheltawy ST. Comparing three options for biodiesel production from waste vegetable oil. WIT Trans Ecol Environ 2008;109:133–40.
[30] Wang J-X, Huang Q-D, Huang F-H, Wang J-W, Huang Q-J. Lipase-catalyzed production of biodiesel from high acid value waste oil using ultrasonic assistant. Chin J Biotechnol 2007;23:121–128.
[31] Armenta RE, Vinatoru M, Burja AM, Kralovec JA, Barrow CJ. Transesterification of fish oil to produce fatty acid ethyl esters using ultrasonic energy. J Am Oil Chem Soc 2007;84:1045–52.
[32] Santos FFP, Malveira JQ, Cruz MGA, Fernandes FAN. Production of biodiesel by ultrasound assisted esterification of *Oreochromis niloticus* oil. Fuel 2010;89:275–9.
[33] Teixeira LSG, Assis JCR, Mendonça DR, Santos ITV, Guimarães PRB, Pontes LAM, et al. Comparison between conventional and ultrasonic preparation of beef tallow biodiesel. Fuel Process Technol 2009;90:1164–6.
[34] Deshmane VG, Gogate PR, Pandit AB. Ultrasound assisted synthesis of isopropyl esters from palm fatty acid distillate. Ultrason Sonochem 2009;16:345–50.
[35] Hanh HD, Dong NT, Okitsu K, Nishimura R, Maeda Y. Biodiesel production by esterification of oleic acid with short-chain alcohols under ultrasonic irradiation condition. Renew Energy 2009;34:780–3.
[36] Kelkar MA, Gogate PR, Pandit AB. Intensification of esterification of acids for synthesis of biodiesel using acoustic and hydrodynamic cavitation. Ultrason Sonochem 2008;15:188–94.
[37] Hanh HD, Dong NT, Okitsu K, Nishimura R, Maeda Y. Test temperature dependence of transesterification of triolein under low-frequency ultrasonic irradiation condition. Jpn J Appl Phys Part 1 2007;46:4771–4.
[38] Hanh HD, Dong NT, Starvarache C, Okitsu K, Maeda Y, Nishimura R. Methanolysis of triolein by low frequency ultrasonic irradiation. Energy Convers Manage 2008;49:276–80.
[39] Hanh HD, Dong NT, Okitsu K, Nishimura R, Maeda Y. Biodiesel production through transesterification of triolein with various alcohols in an ultrasonic field. Renew Energy 2009;34:766–8.
[40] Freedman B, Pryde EH, Mounts TL. Variables affecting the yields of fatty esters from transesterified vegetable oils. J Am Oil Chem Soc 1984;61:1638.
[41] Zhang Y, Dubé MA, McLean DD, Kates M. Biodiesel production from waste cooking oil. 2. Economic assessment and sensitivity analysis. Bioresour Technol 2003;90:229–40.
[42] Kumar D, Kumar G, Poonam CP, Singh. Fast easy ethanolysis of coconut oil for biodiesel production assisted by ultrasonication. Ultrason Sonochem 2010;17:555–9.
[43] Leung DYC, Guo Y. Transesterification of neat and used frying oil: optimization for biodiesel production. Fuel Process Technol 2006;87:883–90.
[44] Stavarache C, Vinatoru M, Maeda Y. Ultrasonic versus silent methylation of vegetable oils. Ultrason Sonochem 2006;13:401–7.
[45] Stavarache C, Vinatoru M, Maeda Y. Aspects of ultrasonically assisted transesterification of various vegetable oils with methanol. Ultrason Sonochem 2007;14:380–6.
[46] Mahamuni NN, Adewuyi YG. Optimization of the synthesis of biodiesel via ultrasound-enhanced base-catalyzed transesterification of soybean oil using a multifrequency ultrasonic reactor. Energy Fuels 2009;23:2757–66.
[47] Mahamuni NN, Adewuyi YG. Application of Taguchi method to investigate the effects of process parameters on the transesterification of soybean oil using high frequency ultrasound. Energy Fuels 2010;24:2120–6.
[48] Colucci JA, Borrero EE, Alape F. Biodiesel from an alkaline transesterification reaction of soybean oil using ultrasonic mixing. J Am Oil Chem Soc 2005;82:525–30.
[49] Avramović JM. The optimization and kinetics of the ultrasound-assisted homogeneous base-catalyzed metanolysis of sunflower oil. PhD. University of Nis, Faculty of Technology, Leskovac; 2011. Submitted for defence (in Serbian).
[50] Refaat AA. Different techniques for the production of biodiesel from waste vegetable oil. Int J Environ Sci Technol 2010;7:183–213.
[51] Thanh LT, Okitsu K, Sadanaga Y, Takenaka N, Maeda Y, Bandow H. Ultrasound-assisted production of biodiesel fuel from vegetable oils in a small scale circulation process. Bioresour Technol 2010;101:639–45.
[52] Fan X, Wang X, Chen F. Ultrasonically assisted production of biodiesel from crude cottonseed oil. Int J Green Energy 2010;7:117–27.
[53] Georgogianni KG, Katsoulidis AK, Pomonis G, Manos PJ, Kontominas MG. Transesterification of rapeseed oil for the production of biodiesel using homogeneous and heterogeneous catalysis. Fuel Process Technol 2009;90:1016–22.
[54] Stavarache C, Vinatoru M, Nishimura R, Maeda Y. Conversion of vegetable oil to biodiesel using ultrasonic irradiation. Chem Lett 2003;32:716–7.
[55] Georgogianni KG, Katsoulidis AK, Pomonis G, Kontominas MG. Transesterification of soybean frying oil to biodiesel using heterogeneous catalysts. Fuel Process Technol 2009;90:671–6.
[56] Cintas P, Mantegna S, Gaudino EC, Cravotto G. A new pilot flow reactor for high-intensity ultrasound irradiation. Application to the synthesis of biodiesel. Ultrason Sonochem 2010;17:985–9.
[57] Povey MJW, Mason TJ. Ultrasound in food processing. London: Blackie Academic & Professionals; 1998. p. 186.
[58] Deng X, Fang Z, Zhang F, Long Y, Yu C. Biodiesel preparation using Jatropha oil by ultrasonic and nanometer catalysts. Trans Chin Soc Agric Eng 2010;26:285–9.
[59] Miladinović MR, Lukić IZ, Stamenković OS, Veljković VB, Skala DU. Heterogeneous base-catalyzed methanolysis of vegetable oils: state of art. Hem Ind 2010;64:63–80.
[60] Thanh LT, Okitsu K, Sadanaga Y, Takenaka N, Maeda Y, Bandow H. A two-step continuous ultrasound assisted production of biodiesel fuel from waste cooking oils: a practical and economical approach to produce high quality biodiesel fuel. Bioresour Technol 2010;101:5394–401.
[61] Helwani Z, Othman MR, Aziz N, Fernando WJN, Kim J. Technologies for production of biodiesel focusing on green catalytic techniques: a review. Fuel Process Technol 2009;90:1502–14.
[62] Helwani Z, Othman MR, Aziz N, Kim J, Fernando WJN. Solid heterogeneous catalysts for transesterification of triacilglycerols with methanol: a review. Appl Catal A 2009;363:1–10.
[63] Mootabadi H, Salamatinia B, Bhatia S, Abdullah AZ. Ultrasonic-assisted biodiesel production process from palm oil using alkaline earth metal oxides as the heterogeneous catalysts. Fuel 2010;89:1818–25.
[64] Verziu M, Comana SM, Richards R, Parvulescu V. Transesterification of vegetable oils over CaO catalysts. Catal Today 2011, doi:10.1016/j.cattod.2010.12.031.

[65] Salamatinia B, Mootabadi H, Bhatia S, Abdullah AZ. Optimization of ultrasonic-assisted heterogeneous biodiesel production from palm oil: a response surface methodology approach. Fuel Process Technol 2010;91:441–8.
[66] Deng X, Fang Z, Hu Y, Zeng H, Liao K, Yu C. Preparation of biodiesel on nano Ca–Mg–Al solid base catalyst under ultrasonic radiation in microaqueous media. Petrochem Technol 2009;38:1071–5.
[67] Qian W-W, Han P-F, Lü X-P. KF/CaO as solid base catalyst for transesterification to biodiesel by ultrasound. Ranliao Huaxue Xuebao 2010;38:52–6.
[68] Ren Q-G, Yan J, Huang G-H, Qiu T-Q, Yang R-F, Fan X-D. Nano KF/γ-Al_2O_3 catalyzed transesterification of soybean oil for biodiesel production by using ultrasonic irradiation. J Cent South Univ (Sci Technol) 2010;41:883–9.
[69] Mason TJ. Sonochemistry. Oxford/New York: Oxford University Press; 1999.
[70] Lin G, Liu H. Ultrasound promoted lipase catalyzed reactions. Tetrahedron Lett 1995;36:6067–8.
[71] Sinisterra JV. Application of ultrasound to biotechnology: an overview. Ultrasonics 1992;30:180–5.
[72] Yu D, Tian L, Wu H, Wang S, Wang Y, Ma D, et al. Ultrasonic irradiation with vibration for biodiesel production from soybean oil by Novozym 435. Process Biochem 2010;45:519–25.
[73] Avramović JM, Stamenković OS, Todorović ZB, Lazić ML, Veljković VB. The optimization of the ultrasound-assisted base-catalyzed sunflower oil methanolysis by a full factorial design. Fuel Process Technol 2010;91:1551–7.
[74] Hernando J, Leton P, Matia MP, Novella JL, Alvarez-Builla J. Biodiesel and FAME synthesis assisted by microwaves: homogeneous batch and flow processes. Fuel 2007;86:1641–4.
[75] Hsiao M-C, Lin C-C, Chang Y-H, Chen L-C. Ultrasonic mixing and closed microwave irradiation-assisted transesterification of soybean oil. Fuel 2010;89:3618–22.
[76] Gogate PR, Pandit AB. A review and assessment of hydrodynamic cavitation as a technology for the future. Ultrason Sonochem 2005;12:21–7.
[77] Fan X, Chen F, Wang X. Ultrasound-assisted synthesis of biodiesel from crude cottonseed oil using response surface methodology. J Oleo Sci 2010;59:235–41.
[78] Noureddini H, Zhu D. Kinetics of transesterification of soybean oil. J Am Oil Chem Soc 1997;74:1457–63.
[79] Vicente G, Martinez M, Aracil J, Esteban A. Kinetics of sunflower oil methanolysis. Ind Eng Chem Res 2005;44:5447–54.
[80] Vicente G, Martinez M, Aracil J. Kinetics of Brassica carinata oil methanolysis. Energy Fuels 2006;20:1722–6.
[81] Marjanović AV, Stamenković OS, Todorović ZB, Lazić ML, Veljković VB. Kinetics of the base-catalyzed sunflower oil ethanolysis. Fuel 2010;89: 665–71.
[82] Stamenković OS, Todorović ZB, Lazić ML, Veljković VB, Skala DU. Kinetics of sunflower oil methanolysis at low temperatures. Bioresour Technol 2008;99:1131–40.
[83] Wang L, Yang J. Transesterification of soybean oil with nano-MgO or not in supercritical and subcritical methanol. Fuel 2007;86:328–33.
[84] Singh AK, Fernando SD. Reaction kinetics of soybean oil transesterification using heterogeneous metal oxide catalysts. Chem Eng Technol 2007;30:1716–20.
[85] Kouzu M, Kasuno T, Tajika M, Sugimoto Y, Yamanaka S, Hidaka J. Calcium oxide as a solid base catalyst for transesterification of soybean oil and its application to biodiesel production. Fuel 2008;87:2798–806.
[86] Veljković VB, Stamenković OS, Todorović ZB, Lazić ML, Skala DU. Kinetics of sunflower oil methanolysis catalyzed by calcium oxide. Fuel 2009;88:1554–62.
[87] Stamenković OS, Veljković VB, Todorović ZB, Lazić ML, Banković-Ilić IB, Skala DU. Modeling the kinetics of calcium hydroxide catalyzed methanolysis of sunflower oil. Bioresour Technol 2010;101:4423–30.
[88] Dossat V, Combes D, Marty A. Lipase-catalysed transesterification of high oleic sunflower oil. Enzyme Microb Technol 2002;30:90–4.
[89] Varma MN, Madras G. Synthesis of biodiesel from castor oil and linseed oil in supercritical fluids. Ind Eng Chem Res 2007;46:1–6.
[90] Torres CF, Moeljadi M, Hill Jr CG. Lipase-catalyzed ethanolysis of fish oils: multi-response kinetics. Biotechnol Bioeng 2003;83:274–81.
[91] Torres CF, Toré AM, Fornari T, Señoráns FJ, Reglero G. Ethanolysis of a waste material from olive oil distillation catalyzed by three different commercial lipases: a kinetic study. Biochem Eng J 2007;34:165–71.
[92] Deshmane VG, Gogate PR, Pandit AB. Ultrasound-assisted synthesis of biodiesel from palm fatty acid distillate. Ind Eng Chem Res 2009;48:7923–7.
[93] Harrington KJ, D'Arcy-Evans C. Transesterification in situ of sunflower seed oil. Ind Eng Chem Prod Res Dev 1985;24:314–8.
[94] Zhang Y, Stanciulescu M, Ikura M. Rapid transesterification of soybean oil with phase transfer catalysts. Appl Catal A: Gen 2009;366:176–83.
[95] Entezari MH, Keshavarzi A. Phase-transfer catalysis and ultrasonic waves. II. Saponification of vegetable oil. Ultrason Sonochem 2001;8:213–6.
[96] Naik SD, Doraiswamy LK. Phase transfer catalysis: chemistry and engineering. AIChE J 1998;44:612–46.
[97] Stamenković IS, Banković-Ilić IB, Stamenković OS, Veljković VB, Skala DU. Continuous biodiesel productions: a review. Hem Ind 2009;63:1–10.
[98] Stavarache C, Vinatoru M, Maeda Y, Bandow H. Ultrasonically driven continuous process for vegetable oil transesterification. Ultrason Sonochem 2007;14:413–7.
[99] Avellaneda F, Salvado J. Continuous transesterification of biodiesel in a helicoidal reactor using recycled oil. Fuel Process Technol 2011;92:83–91.
[100] Thompson LH, Doraiswamy LK. Sonochemistry: science and engineering. Ind Eng Chem Res 1999;38:1215–49.
[101] Kachhwaha SS, Maji S, Faran M, Gupta A, Ramchandran J, Kumar D. Preparation of biodiesel from Jatropha oil using ultrasonic energy. In: Proceedings of the national conference on trends and advances in mechanical engineering. 2006. p. 1–5.
[102] Rodrigues S, Mazzone LCA, Santos FFP, Cruz MGA, Fernandes FAN. Optimization of the production of ethyl esters by ultrasound assisted reaction of soybean oil and ethanol. Braz J Chem Eng 2009;26:361–6.